

SCIENCE FOR CERAMIC PRODUCTION

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FORMATION OF ULTRADISPERSED SYSTEMS BASED ON SODIUM POLYALUMINATES FROM THERMAL PLASMA FLOWS

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The process of synthesis of sodium β -alumina in a low-temperature nitric plasma is investigated. It is established that the main product of the plasmachemical reaction is sodium polyaluminate $\text{Na}_2\text{O} \cdot n\text{Al}_2\text{O}_3$ of an unknown structure, whose homogeneity range is within the interval of $n = 3.5 - 8.0$. The specifics of phase transformations in heating products of plasmachemical synthesis in the temperature interval of $600 - 1400^\circ\text{C}$ are considered. The formation of the phase with the β -alumina structure (β - and β'' - Al_2O_3) proceeds in several stages with the formation of intermediate metastable sodium polyaluminates.

High-density ceramics based on sodium β -alumina is used as a solid electrolyte in thermoelectrochemical generators and batteries with a sodium anode and in other electrochemical devices.

Lately substantial advance has been made in the plasma-chemical synthesis of sodium polyaluminates (SPA) (USSR Inventor's Certif. No. 1510302) [1, 2], which provides vast opportunities for producing a solid electrolyte with high ionic conductivity within the range of compositions depleted in alkali elements. Meeting these requirements is essential for ensuring high electrochemical and corrosion resistance in ceramic electrolytes. A new trend in research is related to the development of thin-film solid electrolytes for thermoelectrochemical generators using plasma spray-deposition methods.

The present study describes the results of studying physicochemical transformations occurring at various stages of plasmachemical synthesis of SPA and identifying the significance of particular reaction parameters for target properties of solid electrolytes.

The development of β -ceramics with high service parameters is closely related to the search for new technologies of synthesis of single-phase materials based on structurally similar modifications of sodium β -alumina of the hexagonal (β - Al_2O_3) and rhombohedral (β'' - Al_2O_3) symmetry with the idealized formulas β - $\text{NaAl}_{11}\text{O}_{17}$ and β'' - NaAl_5O_8 . Their re-

action activity is determined by their chemical and thermal prehistory and mainly by the state of their main component Al_2O_3 participating in the reaction. Therefore, our purpose at the initial state of research was to identify the conditions for the formation of ultradispersed alumina powder from a thermal plasma flow.

The experiments were performed on an experimental plasma test plant for producing oxide powders based on a VChI-63/5.28 IG-L01 high-frequency generator of 105 kW. Nitrogen (or air) was the plasma-forming gas. To increase the degree of dispersion of synthesized products and ensure their complete oxidation, cold air was additionally supplied into the reactor.

The experiments were performed on several SPA compositions with content of sodium oxide varying from 3 to 27% (here and elsewhere wt.%).

The initial materials were aluminum powders, aluminum oxides (or hydroxides), and sodium carbonate (or bicarbonate). Lithium and (or) magnesium oxide additives stabilizing the structure of β'' -polyaluminate were introduced in the amount of 0.7–1.5%. The initial component powders were mixed in a ball mill.

The phase compositions of the products of plasma-chemical synthesis of SPA were analyzed based on x-ray patterns obtained with a DRON-2 diffractometer. The specific surface area of samples was determined using the chromatographic method based on thermal desorption of argon, whereas the shape and size of particles were determined with a ÉMV-100B electron microscope.

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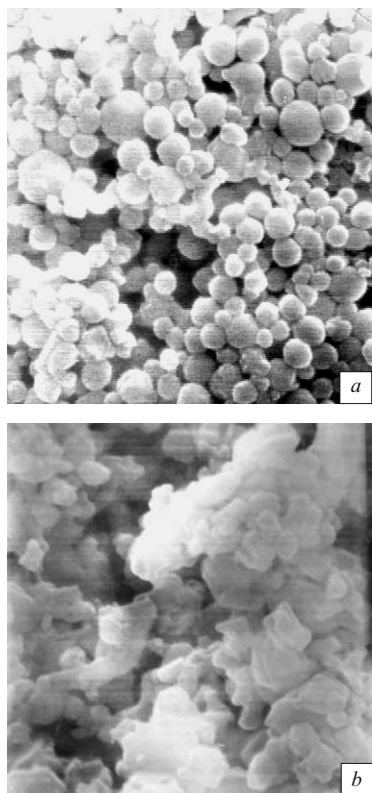


Fig. 1. Electron microscope photos of products (system $\text{Li}_2\text{O} - \text{Na}_2\text{O} - \text{Al}_2\text{O}_3$) of plasmachemical synthesis ($\times 60,000$) before heat treatment (a) and after calcination at 1200°C (b).

The content of sodium in the synthesized products was identified by spectral emission analysis based on characteristic lines of the resonant doublet at $589.0 - 589.9 \mu\text{m}$ using a PAZh-1 plasma analyzer, and the content of lithium was determined using an atom-adsorption spectrometer. The content of oxygen and microimpurities of various elements was determined by neutron-activation analysis. The content of aluminum was identified by the complexonometric method in the presence of a mixed indicator.

In preliminary experiments we studied the conditions of formation of aluminum oxide nanopowders. By means of complete joint evaporation of particles of aluminum and its oxygen compounds in nitrogen plasma at a temperature of $5000 - 5800 \text{ K}$ we obtained ultradispersed aluminum oxide powders with a specific surface area up to $70 \text{ m}^2/\text{g}$.

Based on their phase compositions the synthesized products are attributed to one or several metastable modifications of aluminum oxide based on face-centered cubic packing of oxygen anions: $\gamma\text{-Al}_2\text{O}_3$ with a cubic structure of the spinel type, $\delta\text{-Al}_2\text{O}_3$ of orthorhombic symmetry, and $\theta\text{-Al}_2\text{O}_3$ of monoclinic symmetry.

The synthesis of SPA was performed according to a schedule satisfying the conditions for the formation of ultradisperse alumina powder with a homogeneous phase composition. The products of reactions between the initial compo-

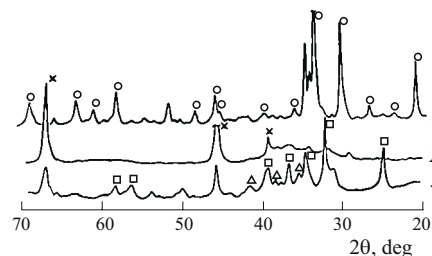


Fig. 2. X-ray patterns of plasmachemical synthesis products in $\text{Na}_2\text{O} - \text{Al}_2\text{O}_3$ system with Na_2O content equal to 26.28% (1), 4.85% (2), and 14.56 % (3): \circ NaAlO_2 ; \square x -phase; \times $\gamma\text{-Al}_2\text{O}_3$; \triangle $\beta''\text{-NaAl}_5\text{O}_8$.

nents in a high-temperature nitrogen flow and their subsequent oxidation constitute SPA nanopowders with a specific surface area of $20 - 30 \text{ m}^2/\text{g}$ consisting of spherical particles. The microphotos of the obtained products of composition (%): 9.0 Na_2O , 0.8 Li_2O , and 90.2 Al_2O_3 are shown in Fig. 1.

The physicochemical properties of some SPA compositions in the $\text{Na}_2\text{O} - \text{Al}_2\text{O}_3$ binary system (obtained from a nitrogen plasma flow with a hardening air flow rate of $5 \text{ m}^3/\text{h}$) are given in Table 1 and their diffraction patterns are shown in Fig. 2. X-ray patterns of samples with a low concentration of sodium exhibit three clear diffraction maxima related to $\gamma\text{-Al}_2\text{O}_3$. The same lines correlate with β'' -aluminate as well; however, the absence of other intense lines typical of this aluminate and the discrepancy of chemical compositions prevent a positive identification of this aluminate under the specified conditions. With a Na_2O content equal to around 6% the diffraction patterns show some more diffraction maxima (Fig. 3) that are impossible to identify. We have designated the corresponding phase as $x\text{-Al}_2\text{O}_3$. With 10 – 15% Na_2O this phase becomes prevalent, whereas β'' sodium aluminate is formed in the products of plasmachemical synthesis when Na_2O content is over 8%. The diffraction maxima of $\beta''\text{-NaAl}_5\text{O}_8$ remain wide and blurred, which is presumably related to the disordered crystalline structure of β'' . With a Na_2O content greater than 15%, part of the products is represented by $\gamma\text{-NaAlO}_2$ monoaluminate, whose content in

TABLE 1

Composition of SPA		Specific surface area, m^2/g	Phase composition
formula	content of Na_2O , %		
$(\text{Na}_2\text{O})_{0.92} \cdot 11\text{Al}_2\text{O}_3$	4.85	24.4	$\gamma\text{-Al}_2\text{O}_3$
$\text{Na}_2\text{O} \cdot 7\text{Al}_2\text{O}_3$	7.95	19.8	$\gamma\text{-Al}_2\text{O}_3$, x
$\text{Na}_2\text{O} \cdot 4.68\text{Al}_2\text{O}_3$	11.46	20.2	x , β'' (traces), $\gamma\text{-Al}_2\text{O}_3$
$\text{Na}_2\text{O} \cdot 3.58\text{Al}_2\text{O}_3$	14.56	23.5	x , β'' (traces)
$\text{Na}_2\text{O} \cdot 2.41\text{Al}_2\text{O}_3$	20.08	19.0	$\gamma\text{-NaAlO}_2$, x , β'' (traces)
$\text{Na}_2\text{O} \cdot 1.71\text{Al}_2\text{O}_3$	26.28	18.3	$\gamma\text{-NaAlO}_2$

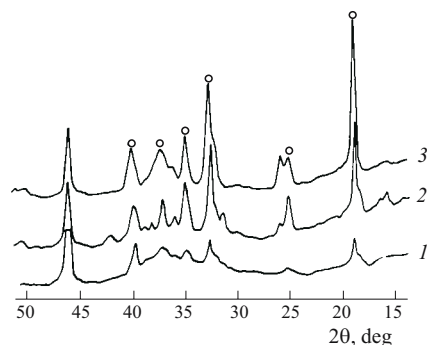


Fig. 3. X-ray patterns of sodium polyaluminates in $\text{Na}_2\text{O} - \text{Al}_2\text{O}_3$ system (1, 2) with Na_2O content equal to 6.2% (1) and 8.5% (2) and in $\text{Li}_2\text{O} - \text{Na}_2\text{O} - \text{Al}_2\text{O}_3$ system (3) with 6.7% Na_2O and 0.8% Li_2O : ○) x -phase.

the mixture grows and becomes prevalent when Na_2O content is above 26%.

The introduction of small additives of lithium or (magnesium) oxides into the system to stabilize the structure of $\beta''\text{-NaAl}_5\text{O}_8$ does not influence the parameters of the plasmachemical process. Therefore, producing SPA in the ternary system $\text{Li}_2\text{O} (\text{MgO}) - \text{Na}_2\text{O} - \text{Al}_2\text{O}_3$ we used the optimal technological procedures determined for the binary system $\text{Na}_2\text{O} - \text{Al}_2\text{O}_3$.

SPA powders obtained in identical conditions in the binary and ternary systems have a similar phase composition. The main difference consists in the fact that small lithium additives accelerate the crystallization of the x -phase. The enhanced ordering of the crystal structure is manifested in the diffraction patterns by a perceptible modification of the intensity of diffraction maxima. A similar modification of diffraction maxima is observed in SPA obtained in the binary system from mixtures with an increased sodium oxide content. At the same time, the intensity of diffraction maxima related to the $\gamma\text{-Al}_2\text{O}_3$ phase decreases.

To study the transformations in SPA under heating, the products of synthesis were calcined in air within a temperature interval of 600 – 1400°C with an exposure for 1 h at the final temperature.

TABLE 2

Firing temperature, °C	Phase composition	
	Al_2O_3	SPA of composition $(\text{Na}_2\text{O})_{1.49} \cdot 5.33\text{Al}_2\text{O}_3$
–	γ, δ	x, β'' (traces)
800	δ, γ, θ (traces)	$x, m\text{-Al}_2\text{O}_3, \beta''$ (traces)
900	δ, γ, θ (traces)	$m\text{-Al}_2\text{O}_3, x, \beta''$ (traces)
1000	δ, θ	$m\text{-Al}_2\text{O}_3, \beta''$
1100	θ, δ	$\beta'', m\text{-Al}_2\text{O}_3$
1200	θ, δ, α (traces)	β''
1300	α	β''
1400	α	β''

Various SPA compositions in the $\text{Na}_2\text{O} - \text{Al}_2\text{O}_3$ binary system undergo ambiguous structural transformations under heating. The initial $\gamma\text{-Al}_2\text{O}_3$ phase in products with a decreased sodium oxide content (not more than 4.5%) is stable up to temperatures of 1300 – 1350°C and then transforms into corundum $\alpha\text{-Al}_2\text{O}_3$ at temperatures above 1350°C. The formation of sodium polyaluminates in such samples has not been registered by x-ray method.

The anomalous behavior of the system in the range of compositions depleted in alkali components is possibly related to the effect of stabilization of the spinel-type structure of $\gamma\text{-Al}_2\text{O}_3$ in the presence of sodium cations. Similar processes have been registered by the authors in [3] studying the specifics of $\gamma\text{-Al}_2\text{O}_3 \rightarrow \alpha\text{-Al}_2\text{O}_3$ phase transition in the presence of monovalent elements of group I. The authors in this case registered the formation of an amorphous phase on the surface of spinel nanoparticles at the initial stage of structural ordering of β -alumina, which delays diffusion processes in $\gamma\text{-Al}_2\text{O}_3$.

Compositions with sodium oxide content ranging from 8 to 20% sometimes exhibit a small quantity of β'' -aluminate in the initial products of synthesis, but the formation of this phase under heating starts within the temperature range of 900 – 1000°C and continues at higher temperatures. At temperatures above 1200°C β'' -aluminate becomes the only phase.

The formation of the β'' -phase proceeds via the formation of metastable sodium polyaluminate $m\text{-Al}_2\text{O}_3$, which is a structural analogue of mullite [4 – 6].

The mullite-like sodium aluminate is present in products of plasmachemical synthesis up to temperatures of 1100 – 1150°C, although the limit of stable existence of $m\text{-Al}_2\text{O}_3$ in solid-phase reactions does not exceed 1050 – 1085°C [5, 6].

The x -phase is absent from SPA compositions with a high content of Na_2O (over 20%) and the formation of β'' -alumina proceeds via monoaluminate $\beta\text{-NaAlO}_2$ which is formed in the temperature range of 850 – 900°C, is the predominant phase in the temperature interval of 900 – 1200°C, and completely transforms into β'' -aluminate at temperatures above 1250 – 1300°C. The formation of the intermediate phase $m\text{-Al}_2\text{O}_3$ has not been registered in such compositions. The two-block β -polyaluminate of hexagonal symmetry has not been registered either. After the specified powder compositions are heat-treated at temperatures above 1300°C, the x-ray patterns exhibit weak lines of β -alumina.

The dynamics of phase transformations of a binary SPA system under heating can be observed taking the composition $(\text{Na}_2\text{O})_{1.49} \cdot 5.33\text{Al}_2\text{O}_3$ as an example. The change in the phase composition of the products of plasmachemical synthesis heated in air up to 1400°C with 1-h exposure (the alumina oxide powder is obtained in a nitrogen plasma under the same conditions) is shown in Table 2.

The analysis of published data suggests that the decisive role in the formation of sodium polyaluminate with a mullite

TABLE 3

Firing temperature, °C	Chemical composition, %; the value n in the formula $\text{Na}_2\text{O}(\text{Li}_2\text{O})_{0-0.24} \cdot n\text{Al}_2\text{O}_3$					
	6.2 Na ₂ O	8.5 Na ₂ O	11.2 Na ₂ O	6.9 Na ₂ O 0.8 Li ₂ O	11.1 Na ₂ O 0.7 Li ₂ O	11.2 Na ₂ O 1.3 Li ₂ O
	$n = 9.20$	$n = 6.55$	$n = 4.83$	$n = 8.15$	$n = 4.83$	$n = 4.74$
—	$\gamma + x$	$x + \beta''$	x	x	x	x
600	Not determ.		x	x	x	Not determ.
800	The same		$x + m$ (traces)	$x + m$ (traces)	$x + m$ (traces)	The same
1000	"		$m + x$ (traces)	$m + x$	$m + x$	"
1100	$\gamma + m + \beta$	$\beta'' + m$	$m + \beta''$	$m + \beta''$	$m + \beta''$	$m + \beta'' + x$
1200	β''	β''	β''	$\beta'' + \beta$	$\beta'' + \beta$	$\beta'' + \beta$
1300	$\beta'' + \beta$ (traces)	β''	—	$\beta'' + \beta$	$\beta'' + \beta$	$\beta'' + \beta$
1400	$\beta'' + \beta$ (traces)	β''	β''	$\beta'' + \beta$	$\beta'' + \beta$	$\beta'' + \beta$

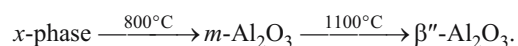
structure belongs to amorphous forms of alumina [5]. It is believed that the tendency for the formation of $m\text{-Al}_2\text{O}_3$ grows with increasing degree of nonequilibrium activity of amorphous alumina in solid-phase reactions with thermally unstable sodium salts.

In this context the question arises whether the regularities established by the authors in [5] for solid-phase reactions extend to plasmachemical processes, considering that physicochemical interactions in thermal plasma flows have a high degree of nonequilibrium. This is corroborated by reports on identifying amorphous forms of alumina together with the γ -modification in aluminum oxide films obtained by plasma spraying.

However, in our experiments sodium polyaluminate with the $m\text{-Al}_2\text{O}_3$ structure mixed with the x -phase has been identified in products of plasmachemical synthesis in insignificant quantities only in SPA samples with a small specific surface area (not greater than $15 \text{ m}^2/\text{g}$) in the presence of Li_2O additives. Such systems are formed from a thermal plasma flow, as a rule, under increased concentrations of the reactants.

The absence of the mullite-like phase in nanosize SPA powders is evidence of a different mechanism of its formation in the products of plasmachemical synthesis. The decisive role in the formation of $m\text{-Al}_2\text{O}_3$ is played, in our opinion, by its metastable sodium polyaluminate precursor with the unknown structure x (Fig. 3), which is the main product of the gaseous-phase reaction.

According to this scheme, the formation of sodium polyaluminate with the mullite structure $m\text{-Al}_2\text{O}_3$ as an intermediate compound occurs in the phase-transformation reactions upon heating nanoproducts of plasmachemical synthesis:



Thus, our results obviously contradict the existing notion of the mechanism of $m\text{-Al}_2\text{O}_3$ formation. The assumptions bellow have been made to resolve the specified contradictions:

The structural formation of the $x\text{-Al}_2\text{O}_3$ polyaluminate takes place not on the surface of the condensed alumina

phases in the zone of contact with the sodium-bearing component, but evolves in the gaseous phase in the reaction flow with subsequent condensation and crystallization of the x -phase; otherwise the reaction between aluminum oxide and the sodium-bearing component would result in the formation of $m\text{-Al}_2\text{O}_3$ or would proceed via the formation of sodium monoaluminate NaAlO_2 , which, according to the conclusions in [5], depends on the state of aluminum oxide, whether it exists in an amorphous form or in the form of any other crystalline modification of Al_2O_3 ; on the other hand, the emergence of the m -phase (in a mechanical mixture with the x -phase) in SPAs obtained in concentrated reaction plasma flows may be evidence of an insufficient degree of mixing the reactants and a possible stratification of condensation aerosols with formation of separate oxide (and oxynitride) forms of the initial components; as the condensed phases were oxidized and hardened in a cold air flow, in this case the amorphous aluminum oxide responsible for the formation of m -polyaluminate may presumably participate in the reaction;

Lithium oxide additives intensify the crystallization of the x -phase and under 1.0 – 1.5% Li_2O stabilize the structure of $x\text{-Al}_2\text{O}_3$ up to a temperature of 1100°C ;

The range of homogeneity of the polyaluminate $\text{Na}_2\text{O} \cdot n\text{Al}_2\text{O}_3$ of the unknown structure x presumably lies within the interval of $n = 3.5 - 8.0$.

The two latter assumptions have been corroborated by the study of the phase transformations of SPA in the system $\text{Li}_2\text{O} - \text{Na}_2\text{O} - \text{Al}_2\text{O}_3$ within the temperature interval of $600 - 1400^\circ\text{C}$. The modification of the phase composition of products of plasmachemical synthesis in the systems $\text{Na}_2\text{O} - \text{Al}_2\text{O}_3$ and $\text{Li}_2\text{O} - \text{Na}_2\text{O} - \text{Al}_2\text{O}_3$ within the temperature interval of $600 - 1400^\circ\text{C}$ is shown in Table 3. For reference purposes, data on the x-ray phase analysis of calcined SPA products for several compositions in the binary system $\text{Na}_2\text{O} - \text{Al}_2\text{O}_3$ are indicated as well in Table 3.

The course of the phase transformations of SPA in the products of synthesis in the systems $\text{Na}_2\text{O} - \text{Al}_2\text{O}_3$ and $\text{Li}_2\text{O} - \text{Na}_2\text{O} - \text{Al}_2\text{O}_3$ under heating is nearly identical. In both cases the initial x -phase persists unchanged up to a tem-

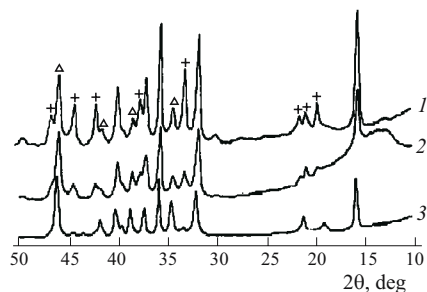


Fig. 4. X-ray patterns of sodium polyaluminate in systems $\text{Li}_2\text{O} - \text{Na}_2\text{O} - \text{Al}_2\text{O}_3$ (1, 2) and $\text{Na}_2\text{O} - \text{Al}_2\text{O}_3$ (3) calcined at 1400°C : 1, 2, 3) 11.1, 6.7, and 11.2% Na_2O , respectively; 1 and 2) 1.3 and 0.8% Li_2O , respectively; +) $\beta\text{-Al}_2\text{O}_3$; Δ) $\beta''\text{-Al}_2\text{O}_3$.

perature of $600 - 700^\circ\text{C}$. At a temperature of 800°C sodium polyaluminate with the mullite structure is formed; at 1000°C the diffraction maxima intensities of the mullite-like phase and the x -phase nearly coincide. At a temperature of 1100°C , apart from the mullite-like phase, the samples also exhibit a certain quantity of β'' -aluminate, whereas the initial x -phase persists only in compositions with an increased content of Li_2O (1.3%).

The main difference between the systems consists in the fact that intense transformation of the polyaluminate x into the mullite phase in the binary system occurs in the range of 900°C ; therefore, $x\text{-Al}_2\text{O}_3$ at 1000°C is virtually absent.

At temperatures above 1200°C hexagonal β -polyaluminate is formed in samples containing lithium oxide, in addition to rhombohedral β'' -polyaluminate.

In samples with equal sodium oxide contents a certain increase in the β'' -phase is observed as the heat treatment temperature grows within an interval of $1200 - 1400^\circ\text{C}$. Diffraction patterns of some SPA compositions calcined at 1400°C are shown in Fig. 4.

Identical regularities of the variations in specific surface area of powders in heating have been established for all the considered products of plasmachemical synthesis, including alumina with different degrees of dispersion and SPA in binary and ternary systems. As the heat treatment temperature increases, the specific surface area of powder decreases (Fig. 5) and, as a rule, is accompanied by a modification of the phase composition.

The break in the dependence plots $S_{\text{sp}} = f(t)$ in the temperature range of $1000 - 1050^\circ\text{C}$ corresponds to the processes of intense structural transformations and the formation of steadier and denser phases. For aluminum oxide the avalanche-like decrease in specific surface area is related to the process of nucleation of $\alpha\text{-Al}_2\text{O}_3$ and subsequent rapid growth of corundum crystals in the sample volume.

The decrease in the specific surface area of SPA is presumably related to the transformation of the orthorhombic structure $m\text{-Al}_2\text{O}_3$ (similar to mullite, but with a doubled axis providing a more symmetric pseudotetragonal structure with cell parameters $a = b = 0.768 \text{ nm}$, $c = 0.291 \text{ nm}$) [6] into the

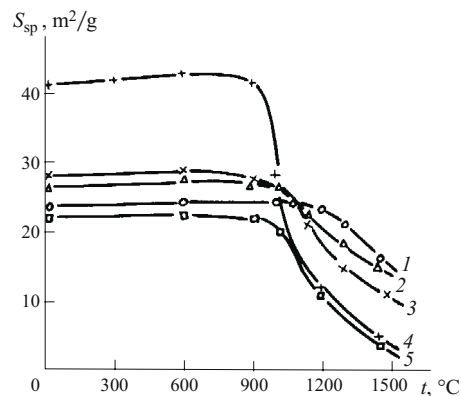


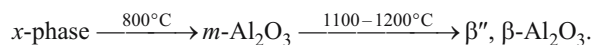
Fig. 5. Dependence of specific surface area S_{sp} of sodium polyaluminate obtained in systems $\text{Li}_2\text{O} - \text{Na}_2\text{O} - \text{Al}_2\text{O}_3$ (1), $\text{MgO} - \text{Na}_2\text{O} - \text{Al}_2\text{O}_3$ (2); $\text{Na}_2\text{O} - \text{Al}_2\text{O}_3$ (3), and aluminum oxides (4, 5) on calcination temperature t (composition, %: 8.60 Na_2O , 0.75 Li_2O , and 0.80 MgO).

rhombohedral structure of β'' -aluminate with hexagonal cell parameters $a = 0.561 \text{ nm}$ and $c = 3.346 \text{ nm}$ (for the composition $\text{Na}_{1.72}\text{Al}_{10.66}\text{Li}_{0.30}\text{O}_{17}$). In this case the phase transformation is accompanied by the SPA density increasing from 2.7 g/cm^3 for the m -phase to 3.28 g/cm^3 for β'' -aluminate.

The rather weak temperature dependence of the specific surface $S_{\text{sp}} = f(t)$ observed within the temperature range below 1200°C for the composites containing lithium oxides also indicates the retardation of the phase transition $m \rightarrow \beta'' + \beta$ with Li_2O additives present.

The results of the studies performed suggest the following.

The process of formation of laminar phases with the β -alumina structure (β'' - and $\beta\text{-Al}_2\text{O}_3$), which are superionic conductors, in sodium polyaluminate powders obtained by plasmachemical synthesis proceeds in several stages with the formation of intermediate metastable SPA modifications that have a similar structure and evolves according to the following scheme:



In compositions with lithium oxide that are of practical interest for the technology of solid electrolytes, the phase transformation of SPA with a specific surface area of $20 - 30 \text{ m}^2/\text{g}$ are completed at higher temperatures with the formation of β -alumina. It should be noted that since the "mullite" polyaluminate is an inhibitor of β -alumina sintering, the presence of the $m\text{-Al}_2\text{O}_3$ phase in SPA powders decreases the density and impairs the service parameters of β -ceramics.

The studies performed have made it possible to identify the specifics of plasmachemical synthesis of sodium polyaluminates and the optimum conditions for the production of powders used in solid electrolyte technology.

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